Proceedings

Intellectual Thermoconductometric Unit Based on Aerosol Printed Ceramic MEMS Sensor for the Measurement of Natural Gas Composition †

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Abstract: The online control of natural gas quality is important for customers, because for them the important value is calorific value of consumed gas, but not its volume. The application of thermoconductometric sensor gives simple possibility to fabricate imbedded intellectual plug-and-play device for this control. The ceramic MEMS sensor based on a combination of this ceramic LTCC membrane and aerosol jet printed platinum microheater was used as a sensing element of this unit. The electronic unit controlling the sensor was designed to stabilize the temperature of the microheater and to measure power necessary to maintain this temperature at different concentrations of $N_2$and CO_2 in natural gas. The application of this unit enables the measurement of admixtures of nitrogen and CO_2 with detection limit of about 1 vol. % sufficient for the application in gas meter instruments.

Keywords: thermoconductometric gas sensor; printing technology; ceramic MEMS; LTCC; natural gas quality

1. Introduction

Natural gas is one of most usable fuels for domestic and industrial application. However, this gas contains often incombustible additives, first of all nitrogen and carbon dioxide. These impurities are supposed to be introduces in a final stage of gas delivery, by gas distribution companies, and, therefore, periodic chromatographic analysis of natural gas doesn't solve this problem. These impurities are supposed to be introduces to the natural gas for increasing total pressure of gas in the "last mile". The main impurities, which are found in natural gas, are nitrogen, N_2, and carbon dioxide, CO_2, the cheapest gases, which could be used for this aim. Of course, online monitoring of the concentration of these additives is important for customers, because they pay not for calorific value of gas, but for the volume consumed by the household. The customer has to believe in the value of calorific value of gas, given by gas supplier. Of course, on-line measurement of calorific value of gas is complicated and expensive. To perform it is absolutely correct way, it is necessary to develop automatic ystem, calorimetric bomb, devoted to determine calorific value of gas. These measurements are not only complicated, but also dangerous, they require addition of oxygen to gas and real combustion/explosion of gas mixture. However, nitrogen or carbon dioxide do not contribute, obviously, to the calorific value of gas. Therefore, indirect estimation of the calorific value of natural gas in pipeline is possible to perform using the heat conductivity of methane/nitrogen mixture as a function of concentration (Figure 1, [1]).

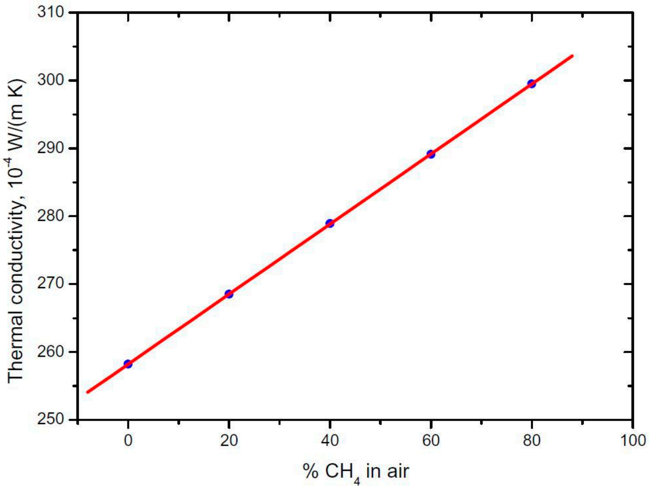
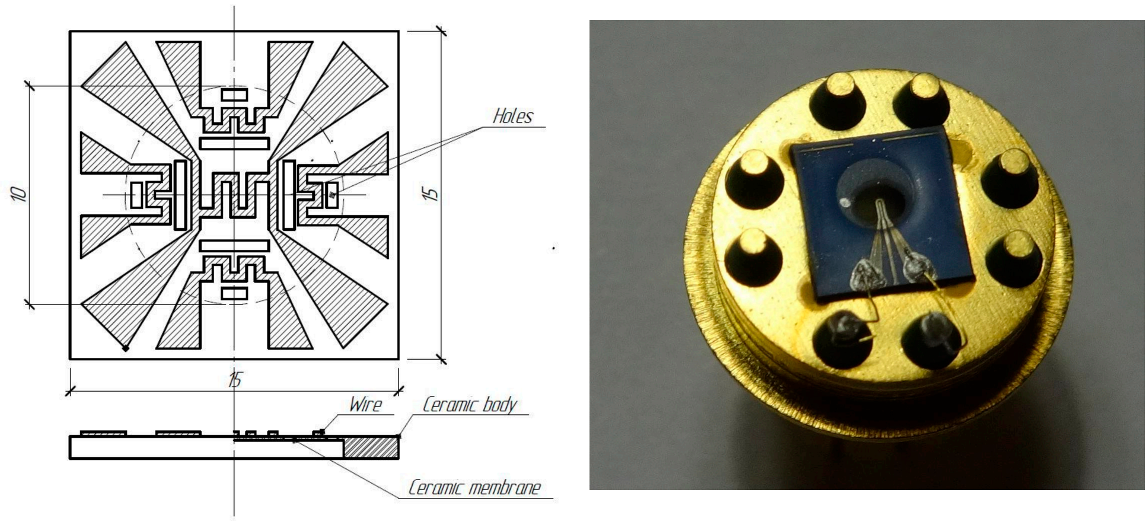


Figure 1. Thermal conductivity of mixture of methane with air at room temperature as a function of methane concentration in the mixture.

2. Experiment

Initially, it was suggested to use sensor design presented in Figure 2A.



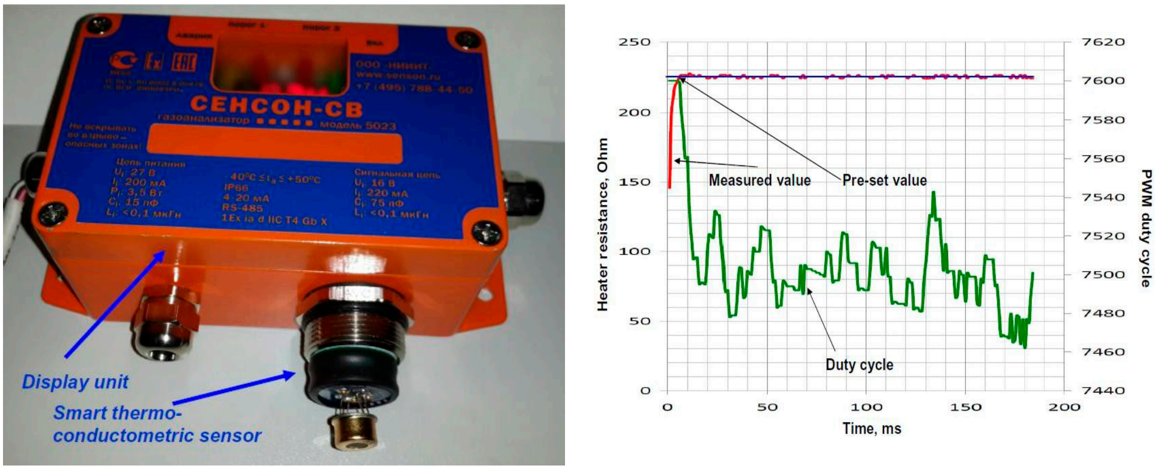
(**A**) (**B**)

Figure 2. (**A**) Initial design of the thermoconductometric gas sensor based on ceramic MEMS. The sensor is a rigid ceramic frame made of 0.5 mm thick ceramics with hole. This hole is covered by thin ceramic film (10–30 μm thick). On the surface of this film using aerosol jet printing platinum microheaters are formed. (**B**) Model thick film thermoconductometric sensor. Working and reference elements are marked in the picture.

It was supposed that the measurement of thermal conductivity will be carried out in impulse mode that is central heater will be heated with short impulse, and then the time delay between this heating impulse and heating of side thermoresistors will be measured. This delay measured by four side thermoresistors depend on gas flow and its thermal conductivity.

The analysis of this sensor design showed that its insufficient reliability. Final sensor design is presented in Figure 2B. The sensor is a ceramic chip, consisting of rigid ceramic frame with hole covered with 10–30 mm thick ceramic membrane. All elements of this chip are made of LTCC ceramics to avoid the problems with difference in thermal expansion coefficients. Microheater is made on the top of the membrane by aerosol jet printing of Pt ink. Power consumption of the microheater at working temperature used in thermoconductometric regime (150 °C) is of ~20 mW.

The controller presented in Figure 3A was used for the stabilization of microheater temperature (150 °C over room temperature in our experiments), for the measurement of power necessary to maintain this temperature, and for the connection to computer using USB. Microheater temperature was stabilized using pulse width modulation (PWM); power was measured as duty cycle of the PW Mheatingprocess. Precision of temperature stabilization is of about 0.1 °C, thermal response time of the sensor with electronic unit is ~50 ms. Temperature stabilization process is presented in Figure 3B. Microcontroller takes into account the variation of heat conductivity as a function of ambient temperature.



(**A**) (**B**)

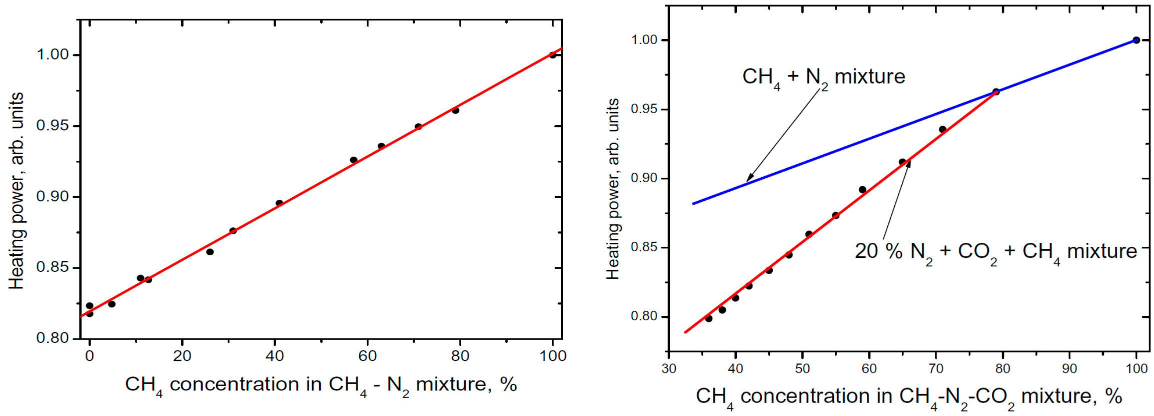
Figure 3. (**A**) Smart sensor unit used for the stabilization of temperature of microheater, measurement of power supplied to the microheater at this stabilized temperature, and for the connection with read-out instrument. (**B**) Heating process of ceramic MEMS gas sensor. Pre-set resistance corresponds to working temperature of 350 °C. 100% duty cycle of PWM corresponds to 8000 value at the right axis. τ_{90} of the heating process is of ~8 ms.

In the experiments, gas mixtures to be tested were prepared by diluting methane with pure nitrogen and CO_2. For this, we used gas mixing set-up equipped with computer-controlled Bronkhorst mass-flow controllers.

3. Results and Discussion

First, preliminary experiments were performed using model thermoconductometric gas sensors. In these sensors the thick film sensing element with size of 2.5 × 0.5 mm was suspended in TO-8 packaging using 20 μm platinum wires. This sensing element was designed in a way that approximately 50% of total heat losses of hot sensing element were due to thermal conductivity of gas medium in the packaging. The sensor chip presented in Figure 2B was compared with this thick film element. The measurements showed that the gas sensing characteristics of this membrane type sensor are close to the characteristics of thick film sensor, and, therefore, the ratio of heat losses through thermal conductivity of air and thermal conductivity of the membrane are also close to 50% for each of heat losses channels. Thus, the sensor based on ceramic membrane is suitable for the measurement of gas concentration using thermoconductometric measurement principle.

The results of the measurement of gas composition of the mixture of CH_4 with N_2 and CO_2 are presented in Figure 4A,B, respectively. Thermal conductivity of N_2 and CO_2 are lower than thermal conductivity of methane (Figure 1) Therefore, power necessary to maintain the same temperature in nitrogen is lower than those in methane approximately by 20% in correspondence with data of Figure 1



(**A**) (**B**)

Figure 4. (**A**) Heating power (sensor signal) as a function of methane concentration in methane—nitrogen gas mixture. Temperature of the microheater is stabilized at 150 °C over room temperature. (**B**) Heating power as a function of CH_4 concentration in CH_4–N_2–CO_2 mixture. N_2 concentration was fixed at 20%, measurements were performed at different concentrations of $CO_2$and CH_4.

The instrument can not distinguish, obviously, between different admixtures in natural gas with heat conductivity lower than those of natural gas; however the precision of the measurement of gas composition is of about ±1 vol. %. This precision is sufficient for the application in measuring devices used for the determination of deviation of gas composition from preset value, because the precision of usual natural gas meter is of 1.5–3%.

4. Conclusions

Plug-and-play thermoconductometric electronic unit designed to stabilize temperature of the sensing element using PWM modulation and measuring power necessary to maintain constant temperature of the microheater is used able for the determination of impurity concentration in naturalgas.TheunitincludesasasensingelementceramicMEMSmicroheatermadeofthis, ~30 µm thick LTCC membrane and aerosol jet printed platinum microheater. The electronic unit with sensor is able to determine impurity concentration with precision of about 1 vol.%.

Author Contributions: A.V. formulated the requirements to the electronic unit, fabricated gas sensing elements, and performed the majority of experiments. I.S. fabricated the electronic plug-and play unit and participated in the experiments. N.S. participated in the fabrication of gas sensors and tested the electronic unit. J.D. formulated general problem and analyzed the results of experiments. P.K. performed the experiments under real working conditions.

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Conflicts of Interest: The authors declare no conflict of interest.

Reference

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